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BEVERIDGE, DEGRANDI, WEILACHER & YOUNG  
INTELLECTUAL PROPERTY GROUP

## SMITH, GAMBRELL &amp; RUSSELL, LLP

ATTORNEYS AT LAW

SUITE 800  
1850 M STREET, N.W.  
WASHINGTON, D.C. 20036

TELEPHONE  
(202) 659-2811  
FACSIMILE  
(202) 659-1462  
WEBSITE  
[www.sgrlaw.com](http://www.sgrlaw.com)

ATLANTA OFFICE  
SUITE 3100, PROMENADE II  
1230 PEACHTREE STREET, N.E.  
ATLANTA, GEORGIA 30309-3592  
(404) 815-3500  
FACSIMILE (404) 815-3509

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Asst. Commissioner of Patents  
Washington, D.C. 20231

**PATENT APPLICATION TRANSMITTAL LETTER**

Inventors: Alain BOUILLOUX et al.

THERMOPLASTIC RESINS MODIFIED BY COPOLYMERS BASED ON  
HEAVY ACRYLATES

Attorney Docket No.: 33808F131 (1798-7361)

Sir:

Transmitted herewith for filing are the following:

New patent application including 21 pages of text, unsigned Declaration, Preliminary Amendment, Information Disclosure Statement, PTO-1449 Form with 7 attached documents and no fees.

Respectfully submitted,  
SMITH, GAMBRELL & RUSSELL, LLP

Beveridge, DeGrandi, Weilacher & Young  
Intellectual Property Group

By:

Frederick F. Calvetti, Reg. No. 28,557  
1850 M Street, N.W., Suite 800  
Washington, D.C. 20036  
Telephone: (202) 659-2811  
Fax: (202) 659-1462

September 26, 2000

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: Alain BOUILLOUX et al.

Serial No.: New Group Art Unit: To Be Assigned

Filed : September 26, 2000 Examiner: To Be Assigned

For : THERMOPLASTIC RESINS MODIFIED BY COPOLYMERS BASED ON HEAVY ACRYLATES

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to or concurrent with calculation of the filing fees, please amend the application as follows.

**IN THE SPECIFICATION:**

Page 1, line 4, change “[Field of the invention]” to --Field of the invention--; and

line 16, change “[Prior art]” to --Background of the Invention--.

Page 2, line 4, change “The Applicant has now” to --It has now been--;

line 10, change “[Brief description of the invention]” to --Summary of the

Invention--; and

line 29, change “[Detailed description of the invention]” to --Detailed

Description of the Invention--.

Page 15, line 9, delete “[Examples]”.

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Page 40, line 15, please add

--Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims. The foregoing references are hereby incorporated by reference.--

**IN THE CLAIMS:**

Please amend claims 1-11 as follows.

Claim 1, line 5, change "chosen" to --selected--.

Claim 2, line 1, change "in which" to --wherein--; and

line 2, change "chosen" to --selected--.

3. (Once Amended) Compositions according to [either of the preceding claims]

Claim 1, wherein [in which] the alkyl of the alkyl (meth)acrylate of (B1) and (B2) has from 5 to 20 carbon atoms [and is preferably 2-ethylhexyl acrylate].

Claim 4, line 1, change "any one of the preceding claims" to --Claim 1--; and

line 2, change "in which" to --wherein--.

5. (Once Amended) Compositions according to [any one of the preceding

claims] Claim 1, wherein [in which advantageously] the proportion of (B) is from 5 to 35 parts per 95 to 65 parts of (M) [and preferably 15 to 25 parts per 85 to 75 parts of (M)].

Claim 6, line 1, change "any one of the preceding claims" to --Claim 1--; and

line 2, change "in which" to --wherein--.

7. (Once Amended) Compositions according to Claim 1 [any one of the preceding claims], wherein [in which] (B) also comprises a functionalized polymer (C1) or a difunctional reactive agent (C2) [so as] to form a crosslinked dispersed phase in the matrix (M).

Claim 8, line 1, change "in which" to --wherein--.

Claim 9, line 1, change "in which" to --wherein--.

10. (Once Amended) Compositions according to [any one of Claims 1 to 6, which comprise] Claim 1, comprising:

- 40 to 97 parts of (M),

- 60 to 3 parts of a dispersed phase comprising:

- 0 to 30 parts of a thermoplastic polymer (D) that differs from (M) and is not

[very] substantially compatible with (M) and

- 3 to 30 parts of (B),

(D) being completely encapsulated in (B).

Claim 11, line 1, change "in which (D) is chosen" to --wherein (D) is selected--.

Please add new claims 12-14 as follows.

--12. (New) Compositions according to Claim 3, wherein acrylate is 2-ethylhexyl acrylate.

13. (New) Compositions according to Claim 5, wherein the proportion of (B) is from 15 to 25 parts per 85 to 75 parts of (M).

14. (New) Compositions according to Claim 11, wherein the polyesters are polyethylene terephthalate, polybutylene terephthalate, and polyethylene naphthenate.--

**REMARKS**

Entry and consideration of this Preliminary Amendment is respectfully requested prior to or concurrent with calculation of the filing fees. This Preliminary Amendment is being filed to remove claims of improper multiple dependency.

Examination on the merits is awaited.

Respectfully submitted,  
SMITH, GAMBRELL & RUSSELL LLP

Beveridge/DeGrandi, Weilacher & Young  
Intellectual Property Group

By: \_\_\_\_\_  
Frederick F. Calvetti, Reg. No. 28,557  
1850 M Street, N.W., Suite 800  
Washington, D.C. 20036  
Telephone: (202) 659-2811  
Fax: (202) 659-1462

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## THERMOPLASTIC RESINS MODIFIED BY COPOLYMERS BASED ON HEAVY ACRYLATES

[Field of the invention]

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The present invention relates to thermoplastic resins modified by copolymers based on heavy acrylates, such as, for example, ethylene/2-ethylhexyl acrylate/maleic anhydride copolymers or ethylene/2-ethylhexyl acrylate copolymers blended with functionalized impact modifiers. The 10 thermoplastic resins are, for example, polyamides, PMMA, polycarbonate or ABS. These modified resins are used to manufacture articles having an improved impact strength. These resins are manufactured by melt blending the various constituents in extruders, mixers (for example, a BUSS® Ko-Kneader) or any other device for blending thermoplastics.

15

[Prior art]

EP 096,264 discloses polyamides having a viscosity of between 2.5 and 5, these being reinforced by ethylene/C<sub>2</sub> to C<sub>8</sub> alkyl 20 (meth)acrylate/unsaturated acid or anhydride copolymers comprising 20 to 40% by weight of acrylate. The heaviest acrylate used in the examples is n-butyl acrylate.

25

US 5,070,145 discloses polyamides reinforced by a blend of (i) a polyethylene or an ethylene/alkyl (meth)acrylate copolymer and of (ii) an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer. As in the previous prior art, the heaviest acrylate used in the examples is n-butyl acrylate.

30

US 4,174,358 discloses reinforced polyamides in the form of a polyamide matrix in which nodules smaller than 1 µm are dispersed, these nodules having a certain modulus which also has to be a fraction of the modulus of the polyamide. Very many reinforcing agents are described, some of them having epoxy functional groups. Most are polymers having neutralized acid or anhydride functional groups or are EPDM-based

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blends. In column 13, polymer 26 is an ethylene/2-ethylhexyl methacrylate/carbon monoxide copolymer, which is used to modify nylon-6,6.

The Applicant has now discovered that if thermoplastic resins are modified by copolymers or blends of copolymers comprising both heavy acrylates and at least one functional group, then impact strengths are obtained which are markedly improved over the prior art. The functional group may be, for example, an anhydride, an acid, an epoxy or an amine.

10 [Brief description of the invention]

The present invention relates to thermoplastic compositions comprising:

15 -40 to 97 parts of a thermoplastic polymer (M) forming a matrix, chosen from polyamides, polyamide block copolymers, fluoro polymers, polycarbonate, styrene resins, PMMA, thermoplastic polyurethanes (TPU), copolymers containing polyester blocks and polyether blocks, polycarbonate-polyester alloys, polyketones, PVC and ethylene-vinyl alcohol copolymers (EVOH),

20 -60 to 3 parts of (B) comprising:

either an ethylene-alkyl (meth)acrylate copolymer (B1), the alkyl having at least 5 carbon atoms, which copolymer (B1) carries a functional group

25 or a blend of an ethylene-alkyl (meth)acrylate copolymer (B2), the alkyl having at least 5 carbon atoms, which copolymer (B2) does not carry a functional group, and of an impact modifier which carries a functional group.

[Detailed description of the invention]

30

The polymers (M) are firstly described; regarding the polyamides, a polyamide should be understood to mean the product of the condensation:

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- of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids or of one or more lactams, such as caprolactam, oenantholactam and lauryllactam;
- 5 - of one or more salts or mixtures of diamines, such as hexamethylenediamine, dodecamethylenediamine, metaxylylenediamine, bis-p(aminocyclohexyl)methane and trimethylhexamethylenediamine with diacids such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic and dodecane dicarboxylic acids;
- 10 - or of mixtures of some of these monomers, thereby resulting in copolyamides, for example PA-6/12 by the condensation of caprolactam with lauryllactam.
- Polymers having polyamide blocks and polyether blocks result from the copolycondensation of polyamide blocks having reactive end groups with polyether blocks having reactive end groups, such as, *inter alia*:
- 15 1) polyamide blocks having diamine chain ends with polyoxyalkylene blocks having dicarboxylic chain ends;
- 20 2) polyamide blocks having dicarboxylic chain ends with polyoxyalkylene blocks having diamine chain ends obtained by cyanoethylation and hydrogenation of aliphatic dihydroxylated alpha,omega-polyoxyalkylene blocks called polyetherdiols;
- 25 3) polyamide blocks having dicarboxylic chain ends with polyetherdiols, the products obtained being, in this particular case, polyetheresteramides.
- The polyamide blocks having dicarboxylic chain ends come, for example, from the condensation of alpha,omega-aminocarboxylic acids, of lactams, or of dicarboxylic acids with diamines in the presence of a chain-stopper dicarboxylic acid. Advantageously, the polyamide blocks are nylon-12 or nylon-6 blocks.
- 30 The number-average molar mass of the polyamide blocks is between 300 and 15,000 and preferably between 600 and 5000. The mass

of the polyether blocks is between 100 and 6000 and preferably between 200 and 3000.

- The polymers having polyamide blocks and polyether blocks may also include randomly distributed units. These polymers may be prepared  
5 by the simultaneous reaction of the polyether and of the polyamide-block precursors.

For example, polyetherdiol, a lactam (or an alpha,omega-amino acid) and a chain-stopper diacid may be reacted in the presence of a little water. A polymer is obtained which has essentially polyether blocks and  
10 polyamide blocks of very variable length, but also the various reactants which, having reacted randomly, are distributed randomly along the polymer chain.

These polymers having polyamide blocks and polyether blocks, whether they come from the copolycondensation of polyamide and  
15 polyether blocks prepared beforehand or from a one-step reaction, have, for example, Shore D hardnesses which may be between 20 and 75, and advantageously between 30 and 70, and an intrinsic viscosity, measured in metacresol at 25°C, of between 0.8 and 2.5.

Whether the polyether blocks derive from polyethylene glycol,  
20 polyoxypropylene glycol or polyoxytetramethylene glycol, they are either used as they are and copolycondensed with polyamide blocks having carboxylic ends, or they are aminated in order to be converted into polyether diamines and condensed with polyamide blocks having carboxylic ends. They may also be blended with polyamide precursors and  
25 a chain stopper in order to make polymers containing polyamide blocks and polyether blocks and having randomly distributed units.

Polymers having polyamide blocks and polyether blocks are disclosed in Patents US 4,331,786, US 4,115,475, US 4,195,015, US 4,839,441, US 4,864,014, US 4,230,838 and US 4,332,920.

30 The polyether may be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG). The latter is also called polytetrahydrofuran (PTHF).

Whether the polyether blocks are introduced into the chain of the polymer containing polyamide blocks and polyether blocks in the form of diols or diamines, they are called, for simplification, PEG blocks or PPG blocks or PTMG blocks.

5 It would not be outside the scope of the invention if the polyether blocks were to contain units different from units derived from ethylene glycol, propylene glycol or tetramethylene glycol.

Advantageously, the polymer containing polyamide blocks and polyether blocks is such that the polyamide is the predominant constituent 10 by weight, that is to say the amount of polyamide which is in block form and that which is possibly distributed randomly in the chain represents 50% by weight or more of the polymer containing polyamide blocks and polyether blocks. Advantageously, the amount of polyamide and the amount of polyether are in the ratio (polyamide/polyether) of 50/50 to 15 80/20.

Preferably, the polyamide blocks and the polyether blocks of the same polymer (B) have  $\bar{M}_n$  masses of 1000/1000, 1300/650, 2000/1000, 2600/650 and 4000/1000, respectively.

By way of examples of fluoro polymers, mention may be made of 20 polyvinylidene fluoride (PVDF), copolymers comprising vinylidene fluoride (VF2), ethylene-tetrafluoroethylene copolymers, poly(trifluoroethylene), trifluoroethylene copolymers, hexafluoropropylene homopolymers and copolymers, and chlorotrifluoroethylene homopolymers and copolymers. Advantageously, PVDF is used.

25 By way of examples of styrene polymers, mention may be made of polystyrene, SAN (styrene/acrylonitrile copolymer), ABS, SAN/ABS alloys and polycarbonate/ABS alloys.

As thermoplastic polyurethanes, mention may be made of 30 polyether urethanes, for example those comprising diisocyanate units, units derived from polyetherdiols and units derived from ethanediol or from 1,4-butanediol. Mention may also be made of polyester urethanes, for example those comprising diisocyanate units, units derived from

amorphous polyester diols and units derived from ethanediol or from 1,4-butanediol.

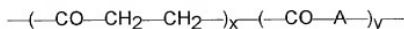
The copolymers containing polyester blocks and polyether blocks are copolymers having polyether units derived from polyetherdiols such as polyethylene glycol (PEG), polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), dicarboxylic acid units such as terephthalic acid and glycol units (ethanediol or 1,4-butanediol). The chain linking of the polyethers and diacids forms the soft segments of the copolyetherester while the chain linking of the glycol or butanediol with the diacids forms the hard segments of the copolyetherester. Such copolyetheresters are disclosed in Patents EP 402,883 and EP 405,227, the contents of which are incorporated in the present application.

By way of examples of polyesters in the polycarbonate/polyester alloys, mention may be made of PET (polyethylene terephthalate), PBT (polybutylene terephthalate) and PEN (polyethylene naphthalene).

The polyketones are polymers comprising substantially one mole of carbon monoxide for each mole of unsaturated monomer. This monomer may be chosen from alpha-olefins having from 2 to 12 carbon atoms or their substitution derivatives. It may also be chosen from styrene or its derivatives obtained by substitution with alkyls such as methyl styrenes, ethyl styrene and isopropyl styrene. Preferably, the polyketones are ethylene-carbon monoxide copolymers or ethylene-propylene-carbon monoxide copolymers.

When the polyketones are copolymers of ethylene, a second monomer and carbon monoxide, there are at least two ethylene units for one unit of the second monomer, and preferably 10 to 100.

The polyketones may be represented by the formula:



in which A denotes an unsaturated monomer having at least 3 carbon atoms, the x/y ratio being at least 2.

The  $\text{---}(\text{CO---CH}_2\text{---CH}_2\text{---})$  and  $\text{---}(\text{CO---A---})$  units are distributed randomly within the polyketone chain.

The number-average molar masses (measured by gel permeation chromatography) may be between 1000 and 200,000, advantageously between 20,000 and 90,000. The melting points may be between 175 and 300°C, usually between 200 and 270°C. Syntheses of these polyketones  
5 are described in Patents US 4,843,144, US 4,880,903 and US 3,694,412, the contents of which are incorporated in the present application.

It would not be outside the scope of the present invention to use a blend of several thermoplastics as (M).

With regard to (B1), the functional group may be attached by  
10 grafting a functional monomer or by copolymerization with this monomer.

By way of examples of functional groups, mention may be made of carboxylic acids and their derivatives, acid chlorides, isocyanates, oxazolines, epoxides, amines and hydroxides.

Examples of unsaturated carboxylic acids are those having 2 to 20  
15 carbon atoms, such as acrylic, methacrylic, maleic, fumaric and itaconic acids. The functional derivatives of these acids comprise, for example, anhydrides, ester derivatives, amide derivatives, imide derivatives and metal salts (such as alkali metal salts) of unsaturated carboxylic acids.

Unsaturated dicarboxylic acids having 4 to 10 carbon atoms and  
20 their functional derivatives, particularly their anhydrides, are particularly preferred monomers.

These monomers comprise, for example, maleic, fumaric, itaconic, citraconic, allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methyl-cyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic  
25 and x-methylbicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acids and maleic, itaconic, citraconic, allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic and x-methylbicyclo[2.2.1]-hept-5-ene-2,2-dicarboxylic anhydrides.

30 Examples of other monomers comprise amide derivatives of unsaturated carboxylic acids, such as acrylamide, methacrylamide, the monoamide of maleic acid, the diamide of maleic acid, the N-monoethylamide of maleic acid, the N,N-diethylamide of maleic acid, the

N—monobutylamide of maleic acid, the N,N-dibutylamide of maleic acid, the monoamide of fumaric acid, the diamide of fumaric acid, the N-monoethylamide of fumaric acid, the N,N-diethylamide of fumaric acid, the N-monobutylamide of fumaric acid and the N,N-dibutylamide of fumaric acid; imide derivatives of unsaturated carboxylic acids, such as maleimide, N-butylmaleimide and N-phenylmaleimide; and metal salts of unsaturated carboxylic acids such as sodium acrylate, sodium methacrylate, potassium acrylate and potassium methacrylate.

Examples of unsaturated epoxides are especially:

- aliphatic glycidyl esters and ethers, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate, glycidyl itaconate, glycidyl acrylate and glycidyl methacrylate, and
- alicyclic glycidyl esters and ethers, such as 2-cyclohexen-1-yl glycidyl ether, diglycidyl cyclohexene-4,5-dicarboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl *endo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate.

Advantageously, the alkyl of the (meth)acrylate has from 5 to 20 carbon atoms. By way of examples, mention may be made of 2-ethylhexyl acrylate (2EHA), n-octyl acrylate and isononyl acrylate. The proportion of (meth)acrylate is advantageously from 5 to 40% by weight of (B1) and the proportion of the functional group is advantageously from 0.1 to 10% by weight of (B1). The MFI of (B1) is advantageously between 0.2 and 40 (at 190°C/2.16 kg). The MFI (the abbreviation for Melt Flow Index) is expressed in g/10 min. Preferably, the functional group is attached by copolymerization of ethylene with (meth)acrylate. These copolymers may be manufactured by radical polymerization in tube reactors or autoclaves at pressures of between 200 and 3000 bar.

With regard to the variant in which (B) comprises (B2) and an impact modifier, (B2) is an ethylene-alkyl (meth)acrylate copolymer, the alkyl having at least 5 carbon atoms. (B2) differs from (B1) only by the absence of a functional group. The MFI of (B2) is advantageously between 0.2 and 40 (190°C/2.16 kg).

The functional group of the impact modifier may be chosen from the same functional groups as those of (B1).

The impact modifier may be a polyolefin chain having polyamide grafts or polyamide oligomers; thus, it exhibits affinity with polyolefins and 5 polyamides.

The impact modifier may also be an ethylene copolymer having maleic anhydride units; thus, it exhibits affinity with polyethylenes and can react with polyamides.

By way of examples of impact modifiers, mention may be made of 10 functionalized polyolefins, grafted aliphatic polyesters, polymers containing polyether blocks and polyamide blocks, optionally grafted, and copolymers of ethylene and a vinyl ester of a saturated carboxylic acid. The copolymers containing polyether blocks and polyamide blocks may be chosen from those mentioned above. They can be used as the polymers 15 (M) and also as a flexibilizer. In the latter case, flexible copolymers, that is to say those having a flexural modulus between 10 and 200 MPa, are chosen instead.

The impact modifier may also be a block copolymer having at least one block compatible with (M) and at least one block compatible with (B2).

20 The functionalized polyolefin is a polymer comprising alpha-olefin units and epoxy or carboxylic acid or carboxylic acid anhydride units.

By way of examples of impact modifiers, mention may be made of 25 polyolefins or SBS, SIS and SEBS block copolymers, EPR (also called EPM) or EPDM, these being grafted by unsaturated epoxides, such as glycidyl (meth)acrylate, or by carboxylic acids, such as (meth)acrylic acid or else by anhydrides of unsaturated carboxylic acids, such as maleic anhydride. EPR denotes ethylene-propylene elastomers and EPDM denotes ethylene-propylene-diene elastomers.

Polyolefin is understood to mean a polymer comprising olefin units 30 such as, for example, ethylene, propylene, 1-butene, or any other alpha-olefin, units. By way of examples, mention may be made of:

- polyethylenes such as LDPE, HDPE, LLDPE or VLDPE,
- polypropylene, ethylene/propylene copolymers or metallocene PEs;

- copolymers of ethylene with at least one product chosen from the salts or esters of unsaturated carboxylic acids, or the vinyl esters of saturated carboxylic acids.

Advantageously, the polyolefin is chosen from LLDPE, VLDPE,  
5 polypropylene, ethylene/vinyl acetate copolymers or ethylene/alkyl  
(meth)acrylate copolymers. The relative density may be advantageously  
between 0.86 and 0.965 and the melt flow index (MFI) may be between 0.3  
and 40.

By way of examples of impact modifiers, mention may also be made of:

- copolymers of ethylene, an unsaturated epoxide and, optionally, an ester or a salt of an unsaturated carboxylic acid or a vinyl ester of a saturated carboxylic acid. These are, for example, ethylene/vinyl acetate/glycidyl (meth)acrylate copolymers or ethylene/alkyl (meth)acrylate/glycidyl (meth)acrylate copolymers;

- copolymers of ethylene, an unsaturated carboxylic acid anhydride and/or a saturated carboxylic acid that may be partially neutralized by a metal (Zn) or an alkali metal (Li) and possibly an ester of an unsaturated carboxylic acid or a vinyl ester of a saturated carboxylic acid. These are, for example, ethylene/vinyl acetate/maleic anhydride copolymers or ethylene/alkyl (meth)acrylate/maleic anhydride copolymers or ethylene/Zn or Li (meth)acrylate/maleic anhydride copolymers;

- polyethylene, polypropylene, ethylene-propylene copolymers grafted or copolymerized with an unsaturated carboxylic acid anhydride and then condensed with a monoaminated polyamide (or a polyamide oligomer). These products are described in EP 342 066.

Advantageously, the functionalized polyolefin is chosen from ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, ethylene/vinyl acetate/maleic anhydride copolymers and ethylene-propylene copolymers containing predominantly propylene, these being grafted by maleic anhydride and then condensed with monoaminated nylon-6 or monoaminated oligomers of caprolactam.

Preferably, it is an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer comprising up to 40% by weight of alkyl (meth)acrylate and up to 10% by weight of maleic anhydride. The alkyl (meth)acrylate may be chosen from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, methyl methacrylate and ethyl methacrylate.

As grafted aliphatic polyesters, mention may be made of polycaprolactone grafted by maleic anhydride, glycidyl methacrylate, vinyl esters or styrene. These products are described in Application EP 10 711,791, the contents of which are incorporated in the present application.

Advantageously, the impact modifier is chosen from ethylene-propylene copolymers (EPR and EPDM) grafted by maleic anhydride, ethylene-alkyl (meth)acrylate-maleic anhydride copolymers, the latter copolymers possibly being blended with ethylene-alkyl (meth)acrylate 15 copolymers, ethylene-alkyl (meth)acrylate/maleic anhydride copolymers blended with (i) ethylene-alkyl (meth)acrylate-glycidyl methacrylate copolymers and (ii) ethylene-alkyl (meth)acrylate-acrylic acid copolymers, the latter three copolymers being crosslinked. These ethylene-alkyl (meth)acrylate-maleic anhydride, ethylene-alkyl (meth)acrylate-glycidyl 20 methacrylate and ethylene-alkyl (meth)acrylate-acrylic acid copolymers may contain up to 40% by weight of acrylate and 10% by weight either of anhydride or of epoxide or of acid. The MFI (melt flow index, is between 2 and 50 g/10 min, measured at 190°C/2.16 kg.

Advantageously, the impact modifier has a flexural modulus of less 25 than 200 MPa and preferably between 10 and 200 MPa.

The proportions of (B2) and of the impact modifier may vary over a wide range and advantageously are in the 80/20 to 20/80 ratio.

The impact strength increases with the amount of (B), the proportion of (B) being advantageously from 5 to 35 parts per 95 to 65 parts of (M) 30 and preferably 15 to 25 parts per 85 to 75 parts of (M).

It would not be outside the scope of the invention to use several copolymers (B1) having identical or different functional groups and,

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likewise, several copolymers (B2) having identical or different functional groups and associated with one or more impact modifiers may be used.

It would not be outside the scope of the invention to add other polymers to (B), such as functionalized or non-functionalized olefin homopolymers or copolymers. By way of examples, mention may be made of ethylene/alkyl (meth)acrylate copolymers whatever the type of alkyl, but alkyl (meth)acrylates having at least 5 carbon atoms, like those described in the present invention, are preferred.

According to a second embodiment of the invention, (B) also comprises a functionalized polymer (C1) or a difunctional reactive agent (C2) so as to form a crosslinked dispersed phase in the matrix (M). The benefit of this crosslinked dispersed phase is that it facilitates its incorporation into the matrix (M) in high amounts, such as 40 to 60%, without the risk of matrix inversion. The advantage of this crosslinked phase, whatever its amount, is that it enables the flexural modulus of the compositions of the invention to be increased. In order to carry out this crosslinking, reactions between carboxylic acid anhydride functional groups and epoxy functional groups are preferred.

With regard to (B) of the (B1) type, (C1) may advantageously be chosen from the impact modifiers already mentioned above, provided that it has functional groups that can react with those of (B1), or from copolymers (B1) provided that it has functional groups that can react with those of (B1) already present. In the latter case, the phase (B) is the product of the reaction of two copolymers (B1) which have different functional groups and can react with each other. Advantageously, (C2) is a dicarboxylic acid, such as adipic acid or dodecanedioic acid, or a diepoxy, such as DGEBA (diglycidyl ether of bisphenol A).

With regard to (B) of the (B2) type as a blend with the impact modifier, (C1) may be chosen from another impact modifier, provided that it has functional groups that can react with those of the impact modifier already present, or from copolymers (B1), provided that it has functional groups that can react with those of the impact modifier. (C2) is as mentioned above.

These crosslinking reactions usually take place according to the stoichiometry of the functional groups in question, and those skilled in the art may therefore readily determine the proportions of (B1), (B2), (C1) or (C2). Advantageously, the reaction between the anhydride functional group and the epoxy functional group is used to form the crosslinked phase.

With regard to the reaction between anhydride and epoxy functional groups, a catalyst may be added. Among compounds capable of accelerating the reaction between the epoxy functional group and the anhydride functional group, mention may be especially made of:

-tertiary amines, such as dimethyltaurylamine, dimethylstearylamine, N-butylmorpholine, N,N-dimethylcyclohexylamine, benzylidemethylamine, pyridine, dimethylamino-4-pyridine, methyl-imidazole, tetramethylethyldihydrazine, N,N-dimethylpiperazine, N,N,N',N'-tetramethyl-1,6-hexanediamine, and a mixture of tertiary amines having from 16 to 18 carbon atoms and known by the name tallow dimethylamine;

-tertiary phosphines, such as triphenylphosphine;

-zinc alkylthiocarbamates.

In this second embodiment of the invention, the reaction between the anhydride and epoxy functional groups is advantageously catalysed by acid functional groups. The Applicant has discovered that some of one (or of several) of the polymers carrying anhydride functional groups need only be replaced with a polymer carrying carboxylic acid functional groups. By way of example, 10 to 70% by weight of an ethylene-alkyl (meth)acrylate-maleic anhydride copolymer containing 3% anhydride may be replaced with the same weight of an ethylene-alkyl (meth)acrylate-(meth)acrylic acid copolymer containing 6% acid. Preferably, this proportion is from 20 to 35%.

According to a third embodiment, the present invention relates to thermoplastic compositions comprising:

- 40 to 97 parts of (M),
- 60 to 3 parts of a dispersed phase comprising:

- 0 to 30 parts of a thermoplastic polymer (D) that differs from (M) and is not very compatible with (M) and
- 3 to 30 parts of (B),

(D) being completely or partly encapsulated in (B).

5        The thermoplastic (D) may be chosen from the family described in the case of (M) but, in addition, also from polyesters such as PET, PBT or PEN. (D) is different, that is to say it is not identical in nature and MFI to (M). For example, if (M) is a PA-6, (D) may be a PA-12. This is because if (D) and (M) are both, for example, PA-12 of the same MFI, the invention is  
10      10 of no benefit. The advantage of this third embodiment of the invention is that it enables nodules of the core-shell type to be incorporated into the matrix (M).

(M) and (D) are chosen so that there is little compatibility between them. Since (D) is dispersed in the matrix of (M) in the form of nodules, (M)  
15      15 and (D) are deemed to be even more incompatible the coarser the nodules of (D). However, it is estimated that if the nodules of (D) are greater than 10 µm there is little compatibility, if the nodules are between 0.5 and 10 µm and preferably between 0.5 and 2 µm there is compatibility, and below 0.5 µm there is very great compatibility.

20        By way of examples of (M)/(D) pairs, mention may be made of:

- . PA-6/PA-12
- . PA-12/PA-11
- . PA-11/PA-12
- . PA-6/PET
- . PA-12/PA-12 of different MFI
- . PA-6/PA-6 of different MFI.

The compositions according to the invention may furthermore contain at least one additive chosen from:

- 30
- dyes;
  - pigments;
  - brighteners;
  - antioxidants;
  - UV stabilizers.

The compositions of the invention are manufactured by melt blending the various constituents (twin-screw extruders, single-screw BUSS®, Ko-Kneader) using the standard techniques for thermoplastics. The compositions may be granulated for the purpose of using them subsequently (they need only be remelted) or else subsequently injected into a mould or an extrusion or coextrusion device for manufacturing pipes, profiles or various articles.

5 [Examples]

10

The following products were used:

- 15 **Ultramid® B3 PA-6:** a nylon-6 of 20 MFI (235°C/2.16 kg) supplied by BASF;
- 15 **Terpol 1:** an ethylene/ethyl acrylate/maleic anhydride terpolymer, of 69.15%/29.5%/1.35% by weight composition respectively, of 6 MFI (190°C/2.16 kg);
- 20 **Terpol 3:** an ethylene/2-ethylhexyl acrylate/maleic anhydride terpolymer, of 69%/30%/1% by weight composition respectively, of 5.5 MFI (190°C/2.16 kg);
- 20 **Terpol 4:** an ethylene/2-ethylhexyl acrylate/maleic anhydride terpolymer of 67%/32%/1% by weight composition respectively, of 6 MFI (190°C/2.16 kg);
- 25 **Terpol 5:** an ethylene/ethyl acrylate/maleic anhydride terpolymer, of 80%/17%/3% by weight composition respectively, of 70 MFI (190°C/2.16 kg);
- 25 **Copol 1:** an ethylene/2-ethylhexyl acrylate copolymer, of 70%/30% by weight composition respectively, of 2 MFI (190°C/2.16 kg);
- 30 **Copol 2:** an ethylene/butyl acrylate copolymer, of 70%/30% by weight composition respectively, of 2 MFI (190°C/2.16 kg).

30

- Examples

In Examples 1 to 3 and 6-7, a 46 mm BUSS® Ko-Kneader is used as a compounding extruder, followed by a rework extruder. The polyamide and terpolymer granules are introduced via feeders into the well 1 of the kneader.

- 5        In Examples 4 to 5, a 40 mm corotating twin-screw (Werner 40) extruder is used as the compounding extruder. The polyamide and terpolymer granules are introduced into the well 1 of the extruder via feeders.
- 10      The base nylon-6 is Ultramid B3 from BASF. Two 2EHA terpolymers (Terpol 3 and Terpol 4) are compared here with an ethyl acrylate terpolymer (Terpol 1). After compounding and granulation, the granules are vacuum-dried at 80°C overnight so as to bring the moisture content measured on the granules down to less than 0.1%. Test pieces in the form  
15 of 80x10x4 mm bars are then injection moulded in order to carry out notched Charpy impact tests (according to the ISO 179/1eA:1994 standard) and to measure the flexural modulus (according to the ISO 178:93 standard). These tests are carried out after a conditioning period of 15 days at 23°C and 50% relative humidity.
- 20      It should be noted that the three terpolymers make it possible to achieve impact properties that are markedly superior to that of the nylon-6 alone. Nevertheless, the performance of both 2EHA terpolymers (Terpol 3 and Terpol 4) is much higher than the EA (ethyl acrylate) terpolymer (Terpol 1).

Table 1

Example No.	1	2	3	4	5	6	7
PA6 (Ultramid B3)	100	80	80	80	80	80	80
Terpol 1		20		20			
Terpol 3			20				
Terpol 4				20			
Copol 2						18	18
Copol 1						2	2
Terpol 5(17% EA/3% MAH)							
Extruder	Buss	Buss	Buss	Twin-screw	Twin-screw	Buss	Buss
Notched Charpy impact strength (ISO 179:94) at +23°C	11	40	112	34	43	50	60
Notched Charpy impact strength (ISO 179:94) at -40°C	2.5	11	16.5	11	17	12	14.5

These are measurements made on test pieces conditioned for 15 days at 50% RH  
 46 mm Buss compounding conditions T° = 230-270°C, speed = 285 rpm, throughput = 20 kg/h  
 40 mm twin-screw (Werner 40) compounding conditions T° = 250-280°C, speed = 300 rpm, throughput = 80 kg/h

## **1 Thermoplastic compositions comprising:**

-40 to 97 parts of a thermoplastic polymer (M) forming a matrix, chosen from polyamides, polyamide block copolymers, fluoro polymers, polycarbonate, styrene resins, PMMA, thermoplastic polyurethanes (TPU), copolymers containing polyester blocks and polyether blocks, polycarbonate-polyester alloys, polyketones, PVC and ethylene-vinyl alcohol copolymers (EVOH),

10 -60 to 3 parts of (B) comprising:

either an ethylene-alkyl (meth)acrylate copolymer (B1), the alkyl having at least 5 carbon atoms, which copolymer (B1) carries a functional group

15 or a blend of an ethylene-alkyl (meth)acrylate copolymer (B2), the alkyl having at least 5 carbon atoms, which copolymer (B2) does not carry a functional group, and of an impact modifier which carries a functional group.

**2** Compositions according to Claim 1, in which the functional group of (B1) and of the impact modifier is chosen from carboxylic acids and their derivatives, acid chlorides, isocyanates, oxazolines, epoxides, amines and hydroxides.

3 Compositions according to either of the preceding claims, in  
25 which the alkyl of the alkyl (meth)acrylate of (B1) and (B2) has from 5 to 20  
carbon atoms and is preferably 2-ethylhexyl acrylate.

4 Compositions according to any one of the preceding claims,  
in which the impact modifier is an ethylene/alkyl (meth)acrylate/maleic  
30 anhydride copolymer.

5 Compositions according to any one of the preceding claims, in which advantageously the proportion of (B) is from 5 to 35 parts per 95 to 65 parts of (M) and preferably 15 to 25 parts per 85 to 75 parts of (M).

5 6 Compositions according to any one of the preceding claims, in which (B) also comprises ethylene/alkyl (meth)acrylate copolymers.

7 Compositions according to any one of the preceding claims, in which (B) also comprises a functionalized polymer (C1) or a difunctional 10 reactive agent (C2) so as to form a crosslinked dispersed phase in the matrix (M).

8 Compositions according to Claim 7, in which the crosslinking of the dispersed phase results from the reaction between an anhydride 15 functional group and an epoxy functional group.

9 Compositions according to Claim 8, in which part of one of the polymers carrying anhydride functional groups is partly replaced with a polymer carrying acid functional groups.

20 10 Compositions according to any one of Claims 1 to 6, which comprise:

- 40 to 97 parts of (M),

- 60 to 3 parts of a dispersed phase comprising:

25 - 0 to 30 parts of a thermoplastic polymer (D) that differs from (M) and is not very compatible with (M) and  
- 3 to 30 parts of (B),

(D) being completely or partly encapsulated in (B).

30 11 Compositions according to Claim 10, in which (D) is chosen from polyamides, polyamide block copolymers, fluoro polymers, polycarbonate, styrene resins, PMMA, thermoplastic polyurethanes (TPU), copolymers containing polyester blocks and polyether blocks,

polycarbonate/polyester alloys, polyketones, PVC and ethylene-vinyl alcohol copolymers (EVOH) and polyesters such as PET, PBT and PEN.

ABSTRACT

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**THERMOPLASTIC RESINS MODIFIED BY COPOLYMERS BASED ON  
HEAVY ACRYLATES**

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**Company named :** ELF ATOCHEM S.A.

4 / 8 Cours Michelet  
92800 PUTEAUX

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**Agent :** Henry NÉEL

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**Inventors :** Alain BOUILLOUX  
Christophe LACROIX  
Jean Marc LE BLEVEC  
Thibaut MONTANARI

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The invention relates to thermoplastic compositions comprising:

-40 to 97 parts of a thermoplastic polymer (M) forming a matrix, chosen from polyamides, polyamide block copolymers, fluoro polymers, polycarbonate, styrene resins, PMMA, thermoplastic polyurethanes (TPU), copolymers containing polyester blocks and polyether blocks, polycarbonate-polyester alloys, polyketones, PVC and ethylene-vinyl alcohol copolymers (EVOH),

-60 to 3 parts of (B) comprising:

either an ethylene-alkyl (meth)acrylate copolymer (B1), the alkyl having at least 5 carbon atoms, which copolymer (B1) carries a functional group

or a blend of an ethylene-alkyl (meth)acrylate copolymer (B2), the alkyl having at least 5 carbon atoms, which copolymer (B2) does not carry a functional group, and of an impact modifier which carries a functional group.

# Declaration and Power of Attorney

## United States Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter which is claimed and for which a patent is sought on the invention entitled

### THERMOPLASTIC RESINS MODIFIED BY COPOLYMERS BASED ON HEAVY ACRYLATES

(check one)  is attached hereto.

- was filed as U.S. Application No. \_\_\_\_\_ on \_\_\_\_\_ and (*if applicable*) was amended on \_\_\_\_\_.
- was filed as PCT International Application No. \_\_\_\_\_ on \_\_\_\_\_ and (*if applicable*) was amended under PCT Article 34 on \_\_\_\_\_.

(I authorize any attorney appointed below to insert information in the preceding blanks.)

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
99.10864	FRANCE	27 AUGUST 1999	NO

I hereby claim the benefit under Title 35, United States Code, §120 or §365(c) of any United States application and PCT international application designating the United States of America listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

I hereby claim priority benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Application No.	Filing Date

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Robert G. Weilacher (20,531), Herbert M. Hanegan (25,682), Frederick F. Calvert (28,557), J. Rodgers Lunsford, III (29,405), Michael A. Makuch (32,263), Dennis C. Rodgers (32,936), William F. Rauchholz (34,701), Michael C. Carrier (42,391), Eric J. Hanson (44,738), Patrick R. Delaney (45,338), Donna D. King (45,962), Joseph M. Lewinski (46,383) and Brandon S. Boss (46,567).

Send all correspondence to: Smith, Gambrell & Russell, LLP, Beveridge, DeGrandi, Weilacher & Young Intellectual Property Group, 1850 M Street, N.W. (Suite 800), Washington, D.C. 20036. All facsimiles may be sent to (202) 659-1462. Direct all phone calls to (202) 659-2811.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor: Alain BOUILLOUX

Citizenship: FRANCE

Residence (city, state, country): Bernay, FRANCE

Post office address: 4, rue du Pont de l'Etang, 27300 Bernay, FRANCE

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Full name of second joint inventor, if any: Christophe LACROIX

Citizenship: FRANCE

Residence (city, state, country): Bernay, FRANCE

Post office address: 29, rue Lobrot, 27300 Bernay, FRANCE

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

\*Additional inventors and/or prior applications are listed in attached Supplemental Sheet(s).

SGR/BDWY

UNITED STATES  
Patents and Design Patents  
Sole & Joint Inventors  
Convention & Non-convention  
PCT & Non-PCT  
This form cannot be amended, altered  
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(For use only for inventors who  
understand the English language.)

Supplemental Sheet to U.S. Declaration and Power of Attorney (SGR/BDWY-1 supp.)

Additional Inventor(s):

Full name of second joint inventor, if any: Jean-Marc LE BLEVEC

Citizenship: FRANCE

Residence (city, state, country): Billiere, FRANCE

Post office address: 5, rue de la Pléiade, Résidence Pyrénées Soleil 3, 64140 Billiere, FRANCE

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Full name of third joint inventor, if any: Thibaut MONTANARI

Citizenship: FRANCE

Residence (city, state, country): Bernay, FRANCE

Post office address: 37, rue Thiers, 27300 Bernay, FRANCE

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Full name of fourth joint inventor, if any:

Citizenship:

Residence (city, state, country):

Post office address:

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Full name of fifth joint inventor, if any:

Citizenship:

Residence (city, state, country):

Post office address:

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Additional Foreign/PCT Applications:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)

Additional U.S. Applications:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

Additional Provisional U.S. Applications:

U.S. Provisional Application No.	Filing Date